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THEORY, MANUFACTURING TECHNOLOGY, AND PROPERTIES OF POWDERS AND FIBERS

DEPENDENCE OF ELECTROLYTIC CELL VOLTAGE ON THE STRUCTURE OF CATHODE DEPOSITS OF PMS11 AND PML0 POWDERS

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The structure of dendritic copper deposit changes during electrolysis: the upper thin elongated branches are finally replaced by coarse globules. Therefore, it is important to determine the period of deposit growth without forming coarse globular particles. This period may be established by analyzing the dynamics of deposit growth and the variation in cathode overpotential, which is a contributor to cell voltage drop and may be used to monitor the structure of cathode deposit. Copper powders PMS11 and PML0 are used to calculate variation in the cell voltage and evaluate the change in deposit structure. The calculations have determined the period of growing homogenous deposits of the copper powders.

Keywords*: copper powder, commercial electrolytic cell, cathode overpotential, cell voltage, deposit growth period.*

INTRODUCTION

In the industry, electrolytic copper powders are produced in galvanostatic conditions. The current applied to the electrolytic cell remains constant, while the cell voltage decreases as the deposit grows. As the current density at the front of growing deposit decreases to the limiting level i_{lim} and lower, there is no longer constraint on the process rate related to the delivery of metal ions to the deposit surface. The transverse microsection of copper deposit in Fig. 1 shows that thin elongated dendrites crystallize at the beginning of electrolysis; their growth rate decreases with time, and large spherulites form at their tips. Joining together, they form a dense metal crust that hinders the removal of the deposit by shaking the cathode. Their formation can be prevented by determining how long the deposit grows before this stage of crystallization begins.

This period can be determined by analyzing the growth of the deposit and the variation of the cathode overpotential, though its continuous measurement in industrial electrolysis conditions involves certain technical

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Fig. 1. Fragment of a section of loose copper deposit on a cylindrical electrode [1]

difficulties. The cathode overpotential is one of the basic components of the voltage drop across the electrolytic cell. The cell voltage can easily be measured and can be used for monitoring the structure of the cathode deposit.

Pomosov [2] was the first to calculate the voltage across the cell for the production of copper powder. He determined the average voltage drop across an electrolytic cell with flat cathodes and an initial cathode current density of 1200 A/m^2. Currently, copper powders are produced in cells with cylindrical cathodes and a current density of 3200 A/m^2. Serebryakov et al. [3] cited statistical data for average current efficiency for some powders and showed how the average cell voltage depended on the concentration of copper ions in electrolyte, temperature, and other factors. However, the average cell voltage does not allow establishing the moment the cathode scrap (dense crust of globular aggregates in the lower part of the rod, which cannot be separated by shaking the cathode) begins to form. To avoid the crystallization of such a deposit, it is necessary to find out what causes its formation, i.e., to study the dynamics of its growth and the time dependence of the overpotential and cell voltage for a specific system (determined by the composition of electrolyte, i.e., grade of the future powder).

The limiting cathode overpotential (0.55–0.59) below which compact copper crystallizes at the growth front was determined in [4] using potentiostatic chronoamperometry.

Analyzing the variation in voltage drop with time and in the radius r_{tip} of dendrite tips makes it possible to determine a period of growing the electrolytic deposit during which there is yet no risk and no inevitable crystallization of dense globular aggregates of cathode scrap. A characteristic of this period, individual for each powder, is the cell voltage corresponding to the limiting cathode overpotential.

Our goal here is calculate and analyze the variation of the voltage across a commercial electrolytic cell for the production of PMS11 and PML0 powders to determine the period of their growth during which no crystallization of dense globular aggregates of cathode scrap occurs.

INITIAL DATA

Electrolysis is carried out in hopper-type cells with one-sided copper busbars, anodes, and rod cathodes. The electrolytic cell has the following characteristics:

Distance between like electrodes	0.15 m
Diameter of cathode rod, d_0	12 mm
Initial average thickness of anode, h	15 mm
Total working surface area of:	
anode, S_a	29.988 m^2
cathode, S_c	3.798 m^2
Current capacity, I.	1200 A

TABLE 1. Initial Parameters of Forming Dendritic Deposits from Solutions Used to Produce PMS11 and PML0 Powders

Parameter	PMS11	PML0
Concentration of copper ions, C (Cu^{2+}), g/L	12.0–13.0	9–10
Conductivity, κ, S/m	85	80
Limiting current density, i_{lim}, A/m^2	270	150
Exchange current density, i_o, A/m^2	17	12
Kinetic coefficient, α	0.535	0.286
Deposit growth period, t, sec	7200	3600

Note: concentration of sulfuric acid 155–165 g/L; temperature T = 323 K; molar volume of copper V_{Cu} = 7.134 × × 10^{-6} m^3/mol.

The composition and properties of electrolyte and the kinetic parameters of producing PMS11 and PML0 powders are presented in Table 1. The kinetic parameters (limiting current density i_{lim}, exchange current i_o, and kinetic coefficient α) were calculated with the semigraphical method, which is used to analyze stationary current–voltage curves for each type of powder. The conductivity of solutions was measured at a temperature of 323 K.

ANALYTICAL

The commercial electrolytic cell operates in galvanostatic mode: current remains constant, while the cell voltage varies with time. This is due to the nature of the process: the greater the diameter of the cathode with deposit (d_0 + 2y), the lower the current density and cathode overpotential. The balance of voltage across an electrolytic cell for the production of dendritic copper deposit is as follows:

$$U(t) = U_{rev} + |\eta_a| + |\eta_c(t)| + \Delta U_{el-t}(t) + \Delta U_{el-d} + \Delta U_{cont}, \quad (1)$$

where $U(t)$ is the electrolytic cell voltage; U_{rev} is the reversible decomposition voltage; $\eta_c(t)$ and η_a are the cathode and anode overpotentials, respectively; $\Delta U_{el-t}(t)$ is the voltage drop across electrolyte; ΔU_{el-d} is the voltage drop across the electrodes; ΔU_{cont} is the voltage drop across contacts and busbars.

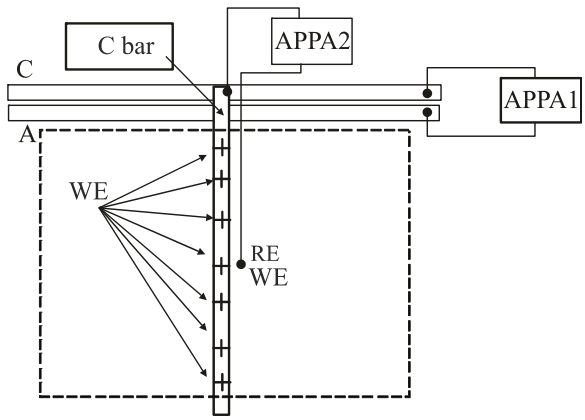

Fig. 2. Measurement of voltage U across the electrolytic cell and cathode overpotential η_c (top view): C—cathode busbar; A—anode busbar; APPA1—high-resistance voltmeter for recording the cell voltage; C bar—one of the 16 cathode bars with cathode rods welded to them from below; WE—working electrode on which the cathode overpotential η_c is measured; RE—reference copper electrode with electric bridge; "+"—coordinates of welding seven copper rods to the cathode bar; APPA2—high-resistance voltmeter for recording the cathode overpotential η_c; dashed—the case of the electrolytic cell

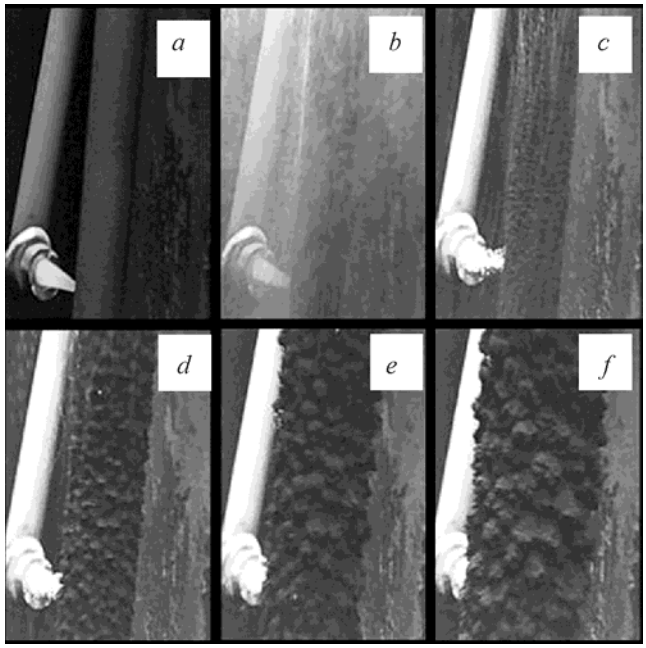

Fig. 3. Still frames from a videorecord of the growth of deposit for PMS11 powder; taken at 0 (*a*), 1 (*b*), 5 (*c*), 30 (*d*), 60 (*e*), and 120 (*f*) min after the beginning of the process

Reversible decomposition voltage is a thermodynamic characteristic (2) calculated using reference data [5]:

$$U_{\text{rev}} = -\frac{\sum \nu_i \cdot \Delta G_i}{z\,\text{F}}, \tag{2}$$

where ΔG is Gibbs energy; F is the Faraday constant (96,500 C/mol); $U_{\text{rev}} = 0.0337$ V

The anodic process involves the mechanism of retarded charge transfer through the interphase boundary, the anodic current density being insignificant and independent of time:

$$\eta_{\text{a}} = \frac{RT}{(1-\alpha)\,z\,\text{F}} \cdot \ln\left(\frac{i_{\text{a}}}{i_{\text{o}}}\right), \tag{3}$$

where i_{a} is the anodic current density, A/m^2.

The time histories of the cathode overpotential $\eta_{\text{c}}(t)$ and the diameter of the cathode with deposit $(d_0 + 2y)$ were obtained in tests in which chronopotentiograms were recorded simultaneously with videorecording of the growth of deposit in a commercial electrolytic cell [6]. Figure 2 shows how the cathode overpotential and cell voltage were measured. The dependence $(d_0 + 2y)(t)$ (Fig. 3) was plotted from still frames obtained by processing the videorecord.

The diameter of the cathode with deposit $(d_0 + 2y)$ constantly increases during electrolysis. The cathode current density $i_{\text{c}}(t)$ decreases because of the increasing area of the deposit growth front. The cathode overpotential is determined by the crystallization conditions for the metal and is continuously measured with an APPA high-resistance voltmeter. The cathode overpotential decreases with the cathode current density (Fig. 4). The curves $\eta_{\text{c}}(t)$ and $(d_0 + 2y)(t)$ are fitted by polynomials (Table 2).

The interelectrode distance l is increased as the deposit growth front moves deep into the solution and is decreased as the anode dissolves:

$$l(t) = \frac{(0.15 - (d_0 + 2y(t))/1000)}{2} - \frac{h}{2} + \frac{dh}{2dt}\int_0^t dt \tag{4}$$

(0.15 is the clear spacing between the cathode and the anode, m).

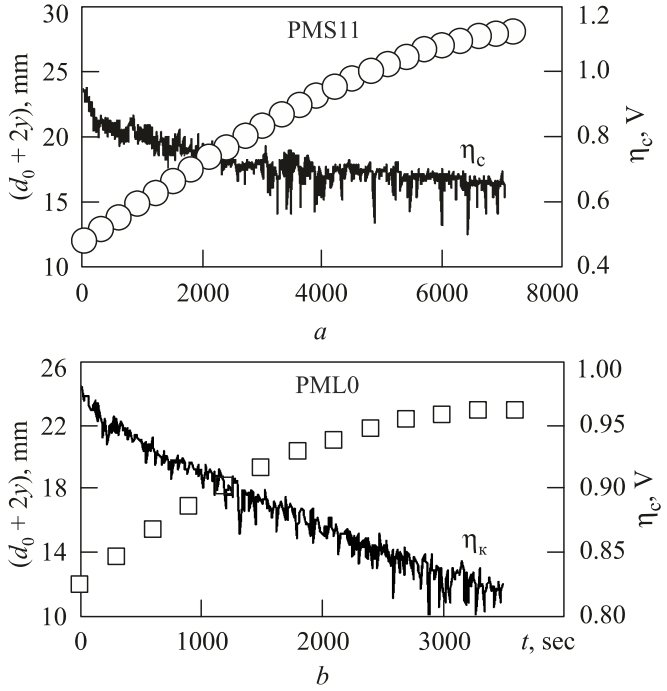

Fig. 4. Chronopotentiograms and variation in the diameter of the cathode with deposit $(d_0 + 2y)$ with time for copper powders PMS11 (*a*) and PML0 (*b*): solid lines—variation of overpotential η_c

TABLE 2. Parameters of Fitted Trends $\eta_c(t)$ and $(d_0 + 2y)(t)$

Function	Fitting polynomial at t = sec
	PML0
$\eta_c = f(t)$	η_c, $V = -9.635 \cdot 10^{-13} \cdot t^3 + 9.442 \cdot 10^{-9} \cdot t^3 + 0.968$
$d_0 + 2y = f_I(t)$	$(d_0 + 2y)$, mm $= -8.699 \cdot 10^{-7} \cdot t^2 + 6.172 \cdot 10^{-3} \cdot t + 12$
	PMS11
$\eta_c = f(t)$	η_c, $V = 6.054 \cdot 10^{-13} \cdot t^3 - 6.571 \cdot 10^{-9} \cdot t^2 - 1.176 \cdot 10^{-5} \cdot t + 0.925$
$d_0 + 2y = \varphi_I(t)$	$(d_0 + 2y)$, mm $= -1.692 \cdot 10^{-11} \cdot t^3 + 2.444 \cdot 10^{-11} \cdot t^3 + 3.099 \cdot 10^{-3} \cdot t + 12$

If the current load is distributed uniformly, it is possible to calculate the dissolution rate for the anode:

$$\frac{dh}{2dt} = \frac{V_{Cu}}{z\,F} \cdot i_a. \tag{5}$$

The resistive components of the electrolyte voltage are calculated from Ohm's law:

$$\Delta U_{el-t}(t) = i_{el-t}(t) \cdot \frac{l(t)}{2}, \tag{6}$$

where $i_{el-t}(t)$ is the average geometrical current density between i_a and i_c:

$$i_{el-t}(t) = \sqrt{i_a \cdot i_c}. \tag{7}$$

The total calculated voltage drop ΔU_{el-d} across the anode and cathode was 0.0004 V.

It is presumed [2] that the voltages across the contacts and busbars, U_{cont}, increase the total cell voltage by 5%.

CALCULATED RESULTS

The time history of cell voltage (Fig. 5) is obtained by summing its components (1).

As the deposit grows, the growth front area increases and the interelectrode distance decreases. This leads to a gradual decrease in the cathode overpotential and the voltage drop across the electrolyte and, as a consequence, to a decrease in the total voltage across the electrolytic cell. The equations of trends $U(t)$ are presented in Table 3.

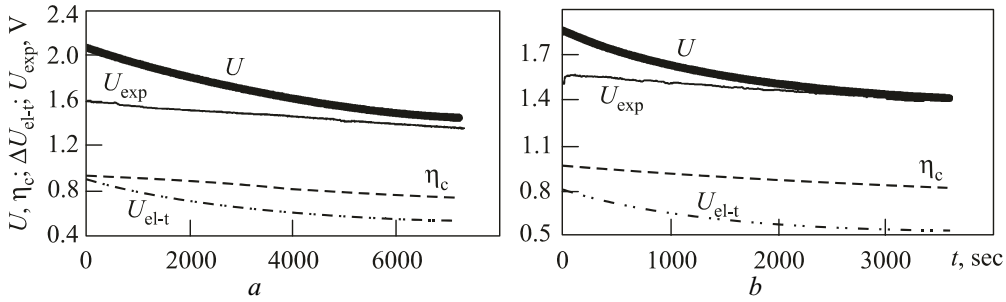

Fig. 5. Calculated (U) balance and measured (U_{exp}) voltage across commercial electrolytic cell for powders PMS11 (*a*) and PML0 (*b*)

TABLE 3. Parameters of Fitted Trends $U(t)$ and $U(\eta_c)$

Function	Fitting polynomial at $\lvert\eta_c\rvert$ = V, $\lvert t\rvert$ = sec	R^2
	PML0	
$U = f(t)$	U, V = $-7.128 \cdot 10^{-12} \cdot t^3 + 7.201 \cdot 10^{-8} \cdot r^2 - 2.926 \cdot 10^{-4} \cdot t + 1.858$	
$U = f_I(\eta_c)$	U, V = $11.613 \cdot \eta_c^2 - 17.784\ \eta_c + 8.193$	1.00
	PMS11	
$U = \varphi(t)$	U, V = $-2.007 \cdot 10^{-14} \cdot t^3 + 8.415 \cdot 10^{-9} \cdot r^{-2} - 1.455 \cdot 10^{-4} \cdot t + 2.066$	
$U = \varphi_I(\eta_c)$	U, V = $752.11 \cdot \eta_c^4 - 2.407 \cdot 10^3 \cdot \eta_c^3 + 2.886 \cdot 10^3 \cdot \eta_c^2 - 1.535 \cdot 10^3 \cdot \eta_c^2 + 306.921$	0.99

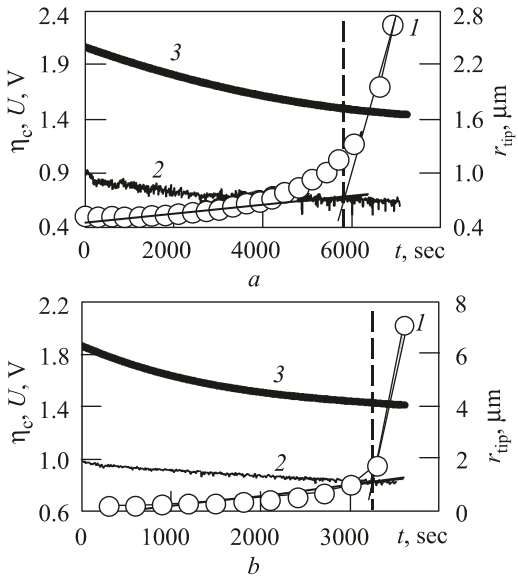

Fig. 6. Curves $r_{tip}(t)$ (*1*), $\eta_c(t)$ (*2*), and $U(t)$ (*3*) for powders PMS11 (*a*) and PML0 (*b*): the dashed line indicates the intersection point of the tangents to the curves $r_{tip}(t)$, being the time point after which the tip radius of the growth front increases abruptly, thus disturbing the uniformity of deposit crystallization

Of special interest is the contribution of the cathode overpotential η_c to the cell voltage. The curve of the cell voltage versus the cathode overpotential is fitted by polynomials for which the coefficients of determination R^2 are known (Table 3). The contribution of the cathode overpotential to the total voltage balance is 49% for PMS11 and 56% for PML0.

As the deposit grows, the diffusion constraints are removed, allowing the tip radius of growing dendrites to quickly increase. The variation of the tip radius with time $r_{tip}(t)$ was calculated considering the mixed nature of cathode reduction of metal at dendrite tips [7].

After the beginning of the process (energizing), the intensive growth of deposit starts in 5900 sec for PMS11 and in 3300 sec for PML0 (Fig. 6). The equations fitting the curve $U(t)$ (Table 3) and the time point after which the intensive growth of dendrites begins were used to calculate the associated cell voltage. It is 1.5 V for PMS11 and 1.42 V for PML0. If $U(t)$ is used for monitoring the structure of the deposit, then after the cell voltage drops to the levels specified above, the nonuniform crystallization of dendrites can be prevented only externally, for example, by reducing the period of growing the dendritic deposit, i.e., by more frequently removing it from the cathode.

The calculated cell voltage U is higher than the experimental value U_{exp} (Fig. 5). The discrepancy is due to the different initial condition of the cathode surface. The calculation was performed for smooth cathode rods with equal initial diameter, whereas, in practice, the removal of the deposit does not recover the initial condition of the cathode surface, and the surface eventually becomes rougher. This causes a lower cathode overpotential and, as a consequence, a lower cell voltage. The calculated and experimental voltages become almost equal in approximately half the period of deposit growth.

CONCLUSIONS

A procedure for the calculation of the voltage across a commercial electrolytic cell from the time history of the cathode overpotential and interelectrode distance for PMS11 and PML0 copper powders has been proposed.

The contribution of η_c into the voltage balance is 49% for PMS11 and 56% for PML0. The coefficient of determination R^2 is 0.99 for PMS11 and 1 for PML0.

By analyzing the dynamics of growing PMS11 and PML0 deposits, the acceptable period of their continuous crystallization has been determined. Polynomials fitting the curve $U(t)$ have been derived.

The critical time points for the function $r_{tip}(t)$ after which deposits begin to grow intensively have been identified: 5900 sec for PMS11 and 3300 sec for PML0.

The time of increase in the radius of particles has been used to determine the cell voltage after which external actions are needed to keep the deposit homogeneous, without the formation of dense globules of cathode scrap.

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